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Characterization of Copper Diffusion in Silicon Solar Cells

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Abstract

In this work we investigate the degradation behavior of solar cells with a copper front side metallization based on a fine-line screen-printed silver seed-layer, a plated nickel diffusion barrier, a plated copper conductive layer and a silver capping. The results reveal that the cell degradation depends, besides the effectiveness of the nickel diffusion barrier, on the used seed-layer and the firing temperature of the seed-layer. The degradation behavior of cells, produced with different Ag seed-layer pastes resulting in different contact finger geometries after screen-printing and firing, was evaluated. With similar nickel diffusion barrier masses the seed-layer that generates the biggest metallized area at the cell surface shows the fastest degradation. Apart from that, the composition of the seed layer also has an impact on the degradation. The analysis of different firing temperatures shows that higher set-peak temperatures result in faster cell degradation due to copper migration.

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Keywords: solar cell metallization; copper; nickel diffusion barrier; long term stability;

1. Introduction and Motivation

Solar cell metallization is the largest individual cost fraction in the costs of solar cell production, dominated by the front silver metallization costs [1]. The substitution of the silver with copper offers the potential to reduce the production costs of silicon solar cells significantly. The copper front side metallization investigated in this work is based on a fine-line screen printed seed layer, a plated nickel diffusion barrier, a plated copper conductive layer, and a thin plated silver capping [2] like it is shown in the microscope cross-section image in Fig. 1.

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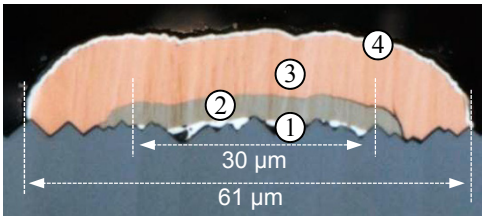

Fig. 1. Microscope cross section image of a contact finger of the copper metallization based on a screen printed fine line silver seed-layer (1) a nickel diffusion (2) barrier, a copper conductive layer (3) and a fine silver capping (4).

This metallization architecture offers the advantage of cost reduction by lowering the total front-side silver consumption to <16 mg per wafer [3]. The effectiveness of the used barrier materials (silicon nitride and nickel) were evaluated in our recent publication [4]. It was found that silicon nitride layers deposited by inline PECVD or inline sputtering avoid copper diffusion into the cell even if pre-treatment with HF dip (1%, 30s prior to copper evaporation) is applied or a high mechanical load is applied during screen-printing (100 N/cm squeegee pressure). We could show additionally that 20 mg plated nickel is sufficient to make long term stability issues due to copper migration improbable in a normal cell lifetime. In this work we present results with respect to influence of the type of applied seed-layer and of the respectively applied firing temperatures on the degradation behavior of the seed- and plate solar cell at elevated temperatures. To characterize the impact of these parameters the rapid cell degradation test at elevated temperatures, published by Bartsch et. al. [5] was used.

2. Experimental

2.1. Solar Cell samples

For the degradation experiments full size (156 x 156 mm^2), p-type, monocrystalline, solar cells were produced by screen printing front-side contacts on textured (random pyramids) Cz silicon wafers with PECVD silicon nitride anti reflection coating, a 90 Ω/sq phosphorous doped emitter and a standard aluminum backside metallization with silver pads. An H-pattern grid with 90 fingers and 3 straight (1.5 mm) or segmented busbars was screen printed on the samples using different silver front side pastes and an industrial, automated inline screen printing machine. The screen openings for the contact fingers were 25µm wide. Depending on the used paste, contacts with different shape were achieved. The samples were fired at set peak temperatures of 860°C, 890°C and 920°C in an inline furnace. Nickel as diffusion barrier, copper as conductive layer and silver as capping layer were plated on the fired contacts using a single side, light induced plating process on inline machines. For nickel plating a Watts-type nickel electrolyte working at a pH of ~4 was used. During this process the backside of the cells does not get in touch with the electrolyte. The nickel mass was varied from 5 mg per cell to 20 mg per cell.

2.2. Cell degradation at elevated temperatures

Cells were heat-treated on hotplates at 175, 200, 225°C, 250°C, and 275°C. The *pFF* was characterized using a Suns Voc measurement setup (Sinton Instruments) with containment to exclude an influence from ambient light. Before each measurement the cells were cooled down to room temperature for two minutes in ambient air. The measurement frequency was adapted to the degradation speed. Average intervals between 4h and 20 h were chosen. The temperature time pairs leading to a *pFF* degradation to 95% of the initial *pFF* value at different temperatures were evaluated using Arrhenius plots. If this value was not exactly measured a linear interpolation between the measured data point above and below 95% were performed to get the desired temperature/time pair.

3. Results

3.1. Influence of the used seed-layer

For the degradation experiments cells with different seed-layer Ag-metallization were used. Fig. 2 shows the average contact finger profiles after firing of three used seed-layers. The contact finger height varies from 1 µm (a) to 9 µm (b). The contact finger width varies from 47 µm (a) to 100 µm (c). The different seed-layer geometries were achieved by using two different pastes. Paste one is a commercial fine line silver paste developed to print fine seed-layers. Paste two and paste three are silver front side pastes based on the same recipe (different from paste one) varied only in the resulting viscosity. Paste two has double the viscosity at a shear rate of 100 s^{-1} (17.6 Pa s compared to 8.5 Pa s) than paste three. This results in different screen printing results.

Table 1 shows the different resulting metallized contact finger areas due to the different contact finger geometries shown in Fig 2 and the metallized busbar area for each paste. The busbar area for paste 2 and 3 is smaller because a segmented busbar design was used. Paste 1 was printed with a standard 1.5 mm busbar design.

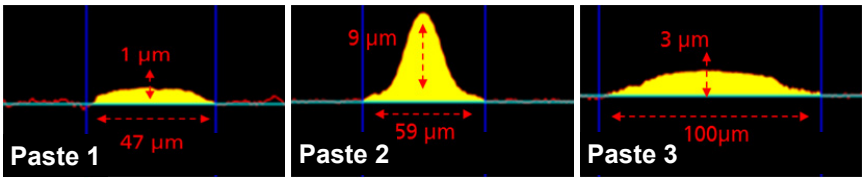

Fig. 2. Profiles of the different used seed-layers after firing. A 47 µm fine and 1 µm thin seed-layer (paste 1), a 9 µm high and 59 µm wide seed-layer (paste 2), and a 3 µm thin and 100 µm wide seed-layer (paste 3).

Table 1. Metalized area at the front-side of the cells for the used Ag pastes.

Paste	Contact finger area / mm^2	Busbar area / mm^2	Total metallized area / mm^2	Total metallized area / %
1	660	664	1324	5.4
2	830	249	1079	4.4
3	1404	249	1653	6.8

The cells were plated with nickel and copper and treated on hotplates as described in section 2.2. Fig. 3 shows the resulting Arrhenius plot for temperature/time pairs leading to a *pFF* degradation to 95% of the original *pFF* value at the different used temperatures with a linear fit through the measured data.

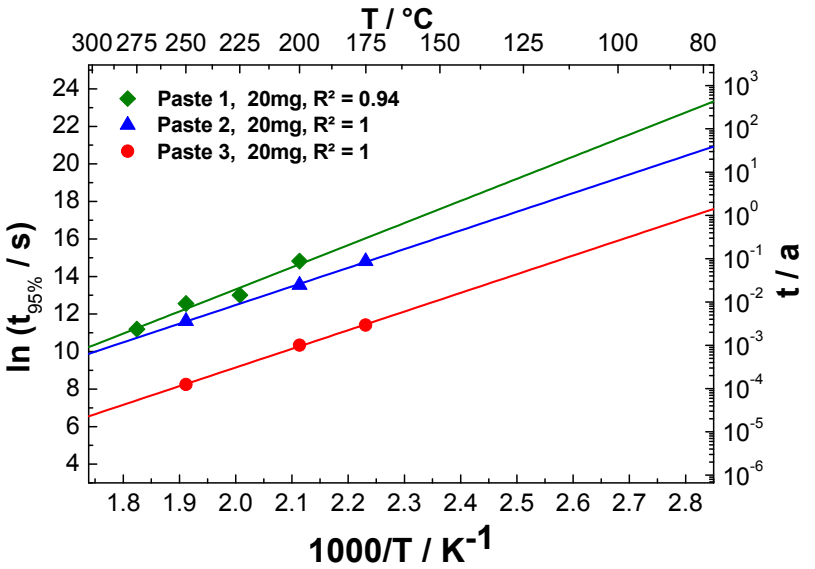

Fig. 3. Arrhenius plot for cells plated with nickel (20 mg) and copper on top of Ag-seed layers with different geometries: paste 1 (green), paste 2 (blue), paste 3 (red) for temperature time pairs leading to a pFF degradation of 5 $\%_{rel.}$.

In general, process differences before temperature treatment can be excluded as reasons behind the different degradation behavior of the cells because the initial *pFF* values for all cells were very similar and ranged between 81.9 and 82.1%. The cells made on the basis of different seed-layers show different degradation behaviour. The seed-layer, which results in the largest metallized area (paste 3), shows the fastest degradation (red circles). This is most probably due to the fact that in the case of paste 3 the same nickel mass was distributed over a bigger metallized area compared to paste 2 (blue triangles). The resulting average nickel layer thickness will be smaller and the probability to get weak points in the nickel diffusion barrier or non-plated areas is higher. Paste 1 (green diamond) shows the best long term stability although the metallized area is bigger than the one of paste 2. Only the metallized finger area corresponds to the degradation result, which may indicate a particularly strong degradation mechanism due to an insufficiently thick barrier at the fingers. Another possible explanation lies in the effect due to differences in the paste formulation.

Additionally the comparison of paste 1 and 2 shows that printing a high silver seed-layer does not necessarily lead to better long term stability results. Although paste 2 offers a longer average diffusion distance for copper to reach the cell than paste 1, due to the higher seed-layer geometry, the long term stability results of paste 1 are better. This means that fine, thin silver seed-layers are not only beneficial to save silver and to reduce shading but also to achieve good long term stability results.

3.2. Influence of the firing temperature

Cells based on a seed-layer of paste 2 and paste 3 were fired at 860°C, 890°C and 920°C and plated as described before with nickel masses of 5 mg, 10 mg and 20 mg per cell. Figure 4 shows the Arrhenius plots for temperature/time pairs leading to a degradation of 5 % $pFF_{rel.}$ For cells plated with 5 mg nickel (green circles), 10 mg nickel (red triangles) and 20 mg nickel (blue squares) for paste 2 (upper diagram) and paste 3 (diagramm below) and all used firing temperatures. Firstly, it is noticeable that all results show a general Arrhenius type trend, which indicates the validity of the method also with a larger set of data. However, the data points for the different groups show clear differences and the regression indicators R^2 are below 93 %, which restricts the prediction quality of the linear fit.

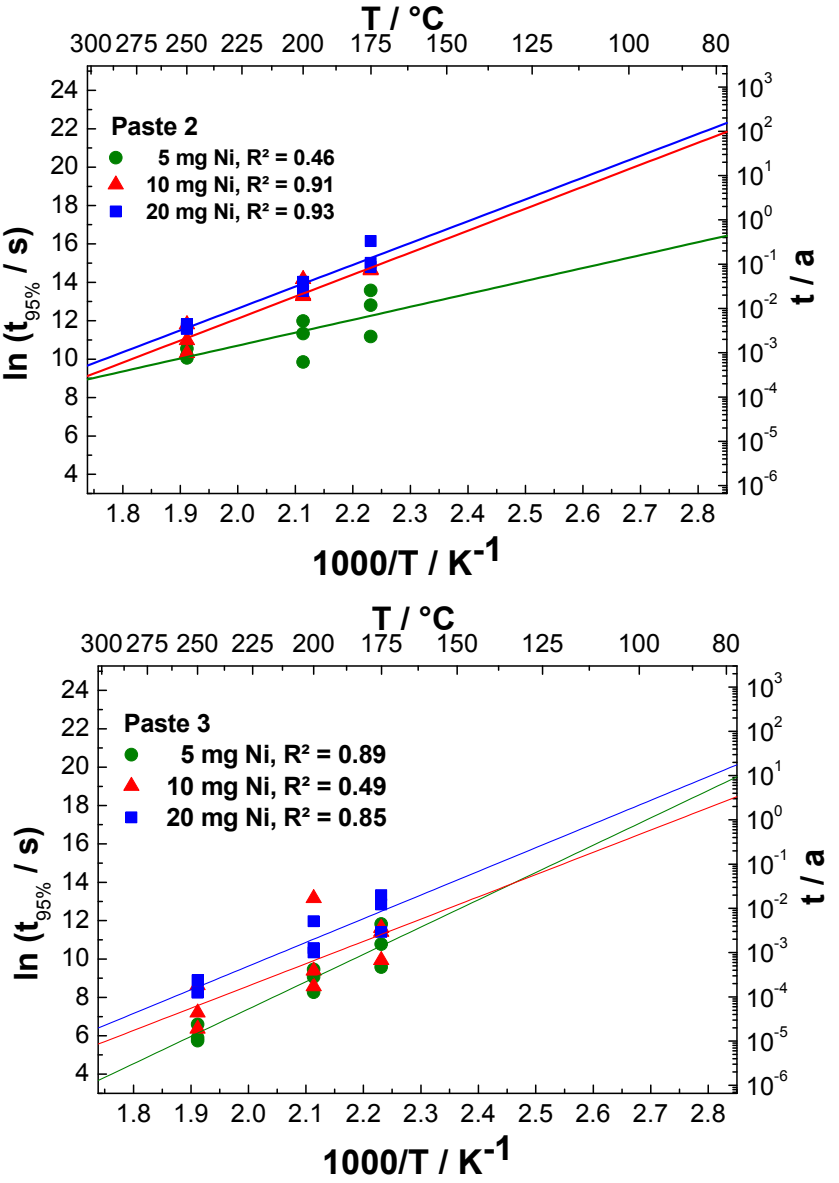

Fig. 4. Arrhenius plot for temperature/time pairs leading to a pFF degradation of 5 %$_{rel.}$ for cells with seed-layer paste 2 (upper diagram) and 3 (lower diagram), plated with 5 mg nickel (green circles), 10 mg nickel (red triangles) and 20 mg nickel (blue squares). Copper and silver plating was constant. The three data points for each measurement represent cells fired at different temperatures.

Figure 5 and 6 show the Arrhenius plots for the same data ordered by firing temperature for every nickel mass for paste 2 (fig 5 a-c) and for paste 3 (fig. 6 a-c). Every diagram in fig. 5 and 6 corresponds to one plated nickel mass: fig. 5 and 6 a) 5 mg Ni, fig. 5 and 6 b) 10 mg, and fig. 5 and 6 c) 20 mg. The unfilled symbols represent the degradation results of the cells fired at a set peak temperature of 920°C, the diagonally crossed symbols show the degradation results of the cells fired at a set peak temperature of 890°C and the filled symbols represent the degradation results of the cells fired at a set-peak temperature of 860°C with linear fit respectively. For paste 2 the regression indicator R^2 for the linear fits are > 93% with two exceptions. For paste 3 the regression indicator R^2 of the linear fits are >96 % with one exception. This is an indication that the deviation observed in figure 4 traces back to a large degree to the different firing temperatures used in the experiment. For paste 2 the graphs for 5 mg plated Ni and 20 mg plated Ni show the fastest degradation for cells fired at 920°C and the slowest degradation for the cells fired at 860°C. For paste 3 this trend can be observed for all plated nickel masses. This is most probably due to a larger opened silicon nitride area under the metal contacts for higher firing temperatures. If copper penetrates the nickel diffusion barrier, the possibility to diffuse into the cell is higher for a bigger opening fraction in the silicon nitride under the contacts. The trend is particularly strong for cells with fast degradation (paste 3 all nickel masses and paste 2 with 5 mg Ni).

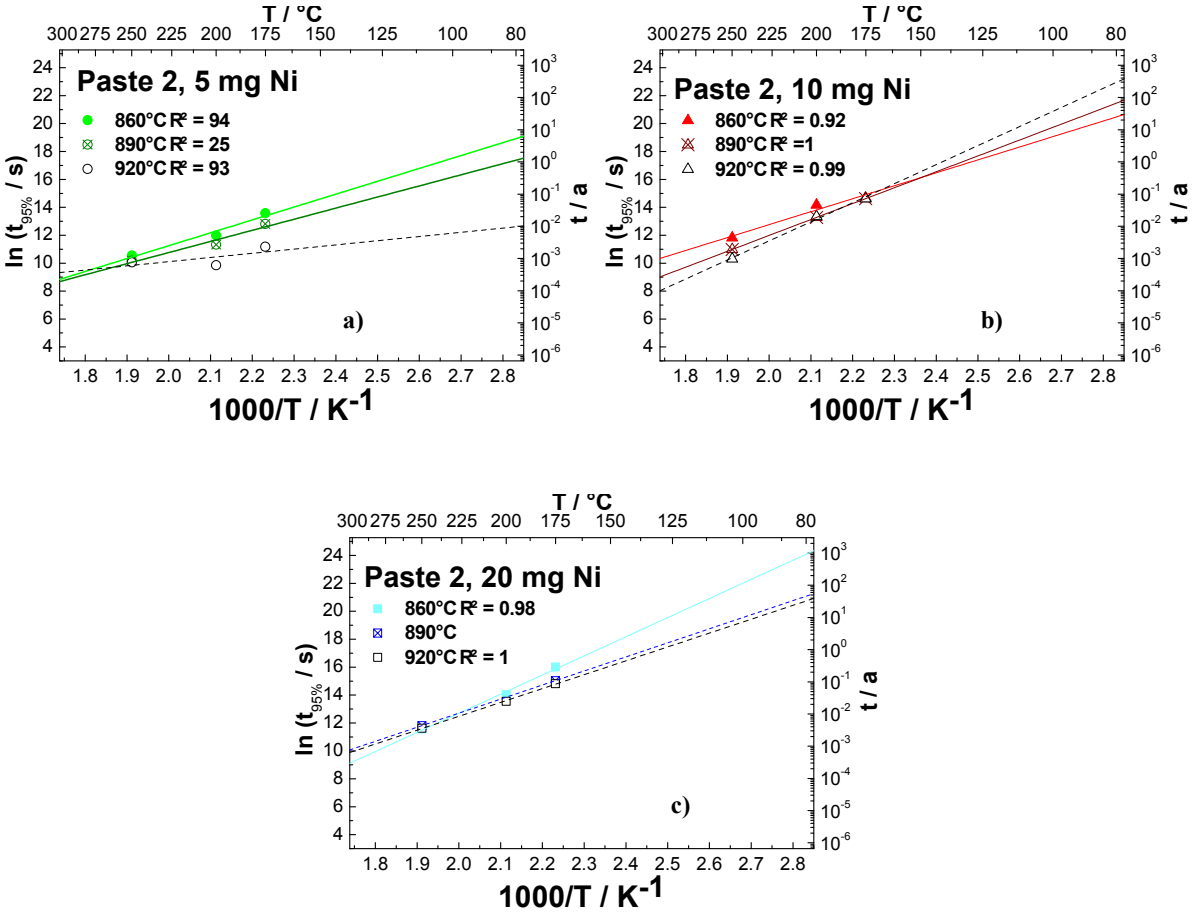

Fig. 5. Arrhenius plots for temperature/time pairs leading to a pFF degradation of 5 $\%_{rel.}$ for cells with seed-layer paste 2 and different firing temperatures, plated with 5 mg nickel (a green data), 10 mg nickel (b red data) and 20 mg nickel (c blue data). The unfilled symbols correspond to the cells fired at 920°C, the diagonally crossed symbols represent the cells fired at 890°C and the filled symbols correspond to the cells fired at 860°C.

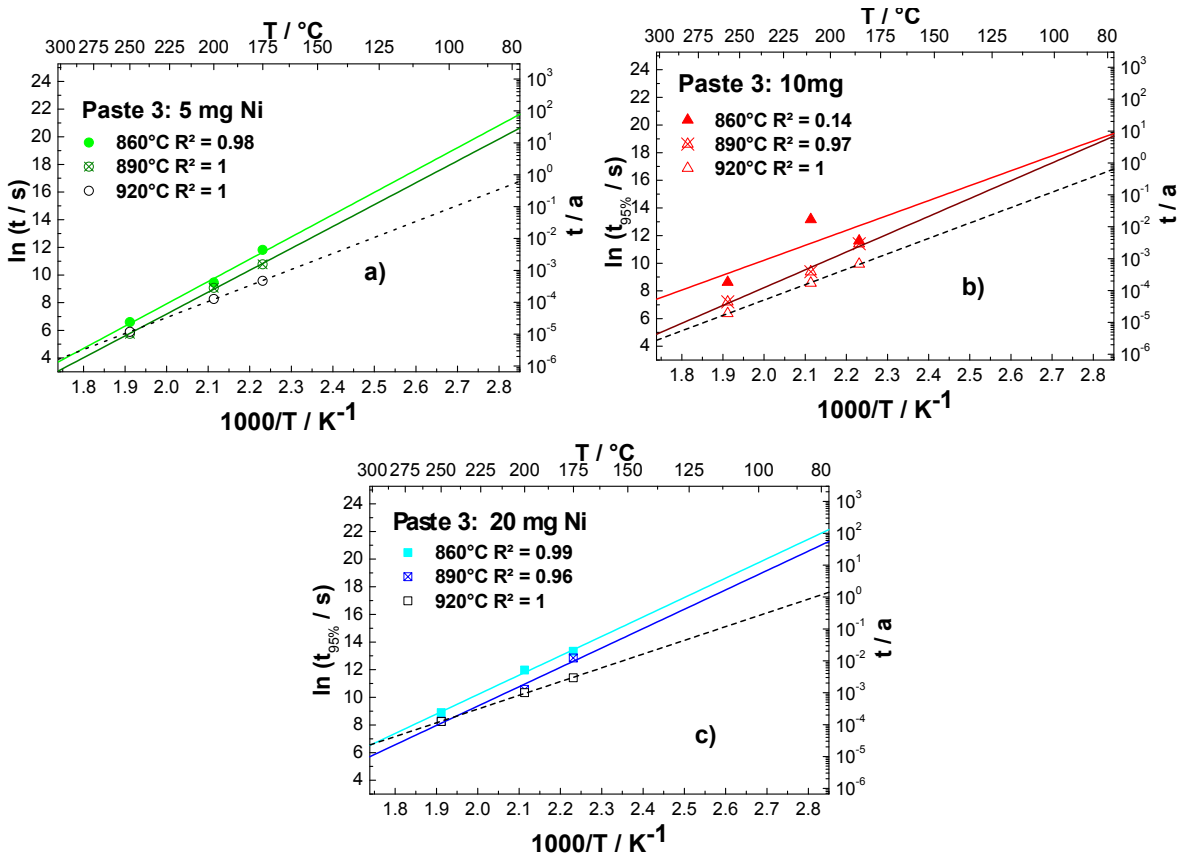

Fig. 6. Arrhenius plots for temperature/time pairs leading to a pFF degradation of 5 $\%_{rel.}$ for cells with seed-layer paste 3 and different firing temperatures, plated with 5 mg nickel (a green data), 10 mg nickel (b red data) and 20 mg nickel (c blue data). The unfilled symbols correspond to the cells fired at 920°C, the diagonally crossed symbols represent the cells fired at 890°C and the filled symbols correspond to the cells fired at 860°C.

4. Conclusion

Analysing the cell degradation of solar cells with a copper front-side metallization based on different silver seed-layers we could show that besides the effectiveness of the nickel diffusion barrier the cell degradation depends on the used seed-layer and the firing temperatures. The seed-layer generating the biggest metallized area shows the fastest degradation comparing cells with identical nickel masses. This means aside from the effect on silver consumption and shading, fine seed layers are also beneficial for long term stability. Despite reports on inhomogeneous plating on wide busbars [6], relatively thin diffusion barriers at this position do not necessarily lead to fast degradation. Possible explanations for this behavior (paste 1 in this work) are a suitable paste composition, or a different interaction at finger positions compared to busbar positions Comparing different firing temperatures the results show that high firing temperatures lead to faster cell degradation. This trend is particularly strong for cell with fast degradation. This is most probably due to a bigger opened silicon nitride fraction under the metallization for higher temperatures.

Acknowledgement

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